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Free-standing Thin Films containing Hexagonally Organized Silver Nanocrystals in a Polymer Matrix

Myong H. Lim and Dieter Ast

Department of Materials Science and Engineering, Cornell University,

Ithaca, New York 14853-1501

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The recent development of nanocomposites consisting of metal nanoparticles embedded in a polymer matrix has spurred broad scientific interest due to several potential applications including optoelectronics, nonliner optical devices[1] and color filters[2]. In these nanocomposites, the nanometer sized metal particles in the polymer matrix exhibit electronic and optical characteristics different from bulk metals, that can be tuned by adjusting the particle size and spacing. The polymer matrix plays a key role in stabilizing nanoparticles as well as enhancing the overall mechanical strength of the film. Techniques to introduce nanoparticles into polymer matrixes have been developed over a past few years[2-7]. However, none of these techniques is capable of generating thin nanocomposite films containing highly ordered periodic arrays of nanoparticles. Although silver nanoparticles have been homogeneously dispersed in polymers by the

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simultaneous or alternative evaporation of silver and polymers[3, 4], the periodicity is poor due to the somewhat broad size distribution as well as the irregular shapes of the particles produced.

A commonly employed method to achieve a narrow size distribution of metallic nanoparticles is to bind organic molecules to their surface to prevent interparticle coagulation or fusion. To produce a uniform particle size, size selective precipitation is necessary. These nearly monodisperse nanoparticles can be used as building blocks to construct 2-D or 3-D organized nanoscopic architectures. Examples include the highly organized 2-D metal quantum dot monolayer films prepared at the air-water interface using Langmuir-Blodgett techniques[8-11], which use the weak van der Waals attractions between adjacent particles for self-assembly. Although these self-assembled monolayer films are transferable to other substrates, there are limitations to their practical utilizations since these LB-films become unstable at the air-water interface after several hours. Moreover, it is difficult to transfer large area LB-films onto various substrates without losing long-range order due to incompatible surface energies. The direct deposition of a solution containing metal nanoparticles is an alternative way to create periodic structures of nanometer-sized particles on solid substrates. However, due to the inability to properly balance the attractive forces between particles and the interactions between the particles and the substrate and the solvent[10, 12], this approach often yields relatively inhomogeneous films consisting of islands of clustered nanoparticles or a multilayer film of fluctuating thickness.

In this communication, we report the successful preparation of novel thin nanocomposite films containing continuous periodic arrays of self-assembled silver

nanocrystals in a polystyrene matrix. In the monolayer areas of the film, the silver nanoparticles are hexagonally arranged. Two different geometrical packings are observed in the bilayer sections. We suggest two schematic models for the interpretations of these interesting patterns.

The formation of the nanocomposite film is carried out at an air-water interface at room temperature in a simple and rapid process. Unlike ordinary LB-films, the preparation of our nanocomposite film does not necessitate any special apparatus, such as a Langmuir trough. To create this nanocomposite film, we first prepared silver nanocrystals with a relatively narrow size distribution using the technique described by Korgel and co-workers[10]. The average size of the silver nanoparticles is approximately 5 nm. To 0.5 mg of these silver nanocrystals in a vial was then added the solution containing 0.3 g of toluene and 0.5 mg of polystyrene with approximate molecular weight of 900,000. The corresponding volume ratio Ag/PS was estimated to be 0.1. The solution was sonicated for 20 minutes to evenly disperse the particles. Approximately 0.5 ml of the resulting solution was then cast on water, contained in a 3-inch petri dish. Evaporation of solvent was slowed by completely covering the dish. Under this condition, toluene molecules escaped from the tiny gap between the dish and its cover. After 1 hour, the toluene evaporation was complete and a shining, wrinkle-free, purple colored nanocomposite film formed on the water surface.

When the film preparation was accelerated by uncovering the dish, the toluene evaporation was non-uniform and wrinkles developed. Flat nanocomposite films can be easily transferred to other substrates without losing continuous nanoscopic periodicity, regardless of the surface energies of these substrates. In addition, freestanding

nanocomposite films can be made by lifting the film with a ring (see figure 1). The good mechanical strength of this very thin film reflects the strong VDW interactions between the polystyrene chains and the thiol-passivated silver nanocrystals as well as polymer chain entanglements. Figure 1 shows a photographic image of a freestanding nanocomposite film supported by a wire loop whose diameter is greater than 1 cm. In optical applications, nanocomposite films are required that posses both mechanical stability and optical transparency. The free-standing nanocomposite film satisfies these requirements.

To investigate its nanoscopic structure, a small portion of the film was torn off using a sharp tweezers, transferred to a regular TEM copper grid, and imaged in a JEOL1200EX Transmission electron microscope (TEM) operating at 120 keV. Figure 2 shows the bright-field TEM image of the nanocomposite film. In this image, two different regions can be seen, which correspond to mono and partial bilayers of silver nanocrystals, respectively. In the monolayer region visible in the center of figure 2, the silver nanocrystals are hexagonally organized, as expected. The hexagonal symmetry of the silver nanocrystal monolayer is further confirmed by Fourier transforming the image, the result of which is shown in the inset picture in figure 2. In the upper and lower regions of the image, two geometrically different patterns are observed. Figure 3a and b displays the enlarged TEM images of these regions. The first pattern in figure 3a shows a combination of local hexagonal ordering, and prolate and triangular shapes. The formation of these patterns implies the stacking of two layers with different unit cell sizes. Figure 3c shows a model that describes the pattern by overlapping two layers, in which the first layer has a slightly greater interparticle distance than the second layer (see Figure

3c). This phenomenon can be rationalized by interfacial tension between the polystyerene film and silver nanocrystals in the first layer, which affects the interparticle distance between silver nanocrystals as well as overall geometrical ordering. The second observed pattern shown in Figure 3b exhibits a series of "donut" ring shapes, which is analogous to a rotational Moiré pattern[13], but the unit cell size of second layer is smaller than that of the first layer, as indicated. Figure 3d elucidates the formation of this pattern, which illustrates that the second layer with a smaller interparitcle distance is rotated 30° with respect to the first layer. Additionally, the 2-D Fourier transform image of figure 3b supports the model in figure 3d by exhibiting an imprecise 12-fold symmetry that results from two six-fold symmetries rotated by 30° relative to each other.

A careful examination of the TEM images indicated that a continuous polystyrene thin film underlies the silver nanocrystals. This was confirmed by imaging a film where the silver nanocrystals were removed by a 37 % HCl etch. The TEM image of the etched film was featureless, implying that the silver nanocrystals rest on the surface of polystyrene films. At the water-air interface, thin film formation is regulated by surface energies, i.e., the degree of interfacial affinity[14]. Thus, if polystyrene has lower surface energy with water than thiol-passivated silver nanocrystals, a continuous polystyrene film will form first. In our control experiment, polystyrene itself could not form a uniformly spread thin film at air-water interface because of the relatively large repulsion force between the hydrophobic polystyrene and hydrophilic water surface. Similarly, thiol-passivated silver nanocrystals by themselves produced partially arrayed thin films, which dissociated within a couple of hours. Thus, the formation of large area of thin nanocomposite films results from cooperative assembly of these silver nanocrystals and

polystyrene, due to the strong hydrophobic attractions between polystyrene chains and thiol-passivated silver nanocrystals as well as between the polystyrene chains themselves. The attractive interactions between polystyrene chains floating on water influence the assembly of the silver nanocrystals adsorbed on their hydrophobic chains, which generates the periodic array of silver nanocrystal superlattices. These chemical forces seem to play a similar role as the external force applied in the LB-technique.

In conclusion, we describe an efficient method for synthesizing thin silver-polystyrene nanocomposite films possessing highly ordered silver nanocrystal superlattices. Owing to polystyrene matrix, the thin nanocomposite film can be freestanding, and also can be easily transferred on various substrates regardless of their surface energies. Two characteristic geometrical bilayer patterns were observed, which offer many new opportunities in the nanomaterial fabrications of size-selected quantum dot materials. The simple and rapid synthetic procedure described here should be applicable to a variety of metal or semiconductor-polymer nanocomposite systems.

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References

[1] A. Heilmann, J. Werner, D. Schwarzenberg, S. Henkel, P. Grosse, W. Theiss, *Thin Solid Films 270* (1995) 103.

[2] Y. Dirix, C. Bastiaansen, W. Caseri, P. Smith, *Adv. Mater. 11* (1999) 223.

[3] A. Heilmann, J. Werner, *Thin Solid Films 317* (1998) 21.

[4] K. Akamatsu, S. Takei, M. Mizuhata, A. Kajinami, S. Deki, S. Takeoka, M. Fujii, S. Hayashi, K. Yamamoto, *Thin Solid Films 359* (2000) 55.

[5] Y. J. Zhu, Y. T. Qian, X. J. Li, M. W. Zhang, *Nanostructured Materials 10* (1998) 673.

[6] Y. D. Yin, X. L. Xu, C. J. Xia, X. W. Ge, Z. C. Zhang, *Chem. Commun.* (1998) 941.

[7] C. W. Chen, M. Q. Chen, T. Serizawa, M. Akashi, *Adv. Mater. 10* (1998) 1122.

[8] S. A. Harfenist, Z. L. Wang, M. M. Alvarez, I. Vezmar, R. L. Whetten, *J. Phys. Chem. 100* (1996) 13904.

[9] J. R. Heath, C. M. Knobler, D. V. Leff, *J. Phys. Chem. B 101* (1997) 189.

[10] B. A. Korgel, S. Fullam, S. Connolly, D. Fitzmaurice, *J. Phys. Chem. B 102* (1998) 8379.

[11] X. Y. Chen, J. R. Li, L. Jiang, *Nanotechnology 11* (2000) 108.

[12] B. A. Korgel, D. Fitzmaurice, *Physical Review Letters 80* (1998) 3531.

[13] D. B. Williams, C. B. Carter, *Transmission electron microscopy : a textbook for materials science*, Plenum Press, New York 1996.

[14] K. Tsujii, *Surface activity : principles, phenomena, and applications*, Academic Press, San Diego 1998.

Captions

Figure 1. Photograph image of a thin nanocomposite Ag-PS film supported by a wire loop

Figure 2. Bright field TEM image of the nanocomposite Ag-PS film. Regions of mono & and bilayers can be observed. The inset image is a Fourier transform of the image. (Scare bar = 100 nm)

Figure 3. a) Enlarged TEM image of the lower region of fig 2, b) Enlarged TEM image of the upper region of fig 2. c) A generated bilayer model by stacking two nanocrystal packed layers in which the upper layer has a smaller interparticle distance. d) Another bilayer model by stacking two layers in which the upper layer has a smaller interparticle distance rotated 30° with respect to each other. The inset images are a Fourier transform of the image.

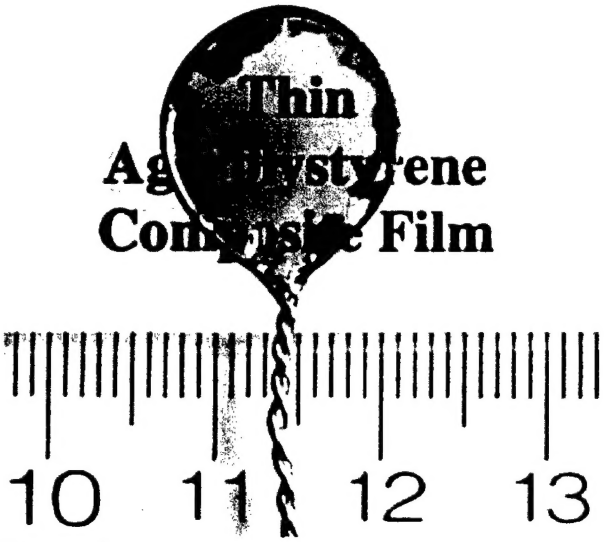


Figure 1

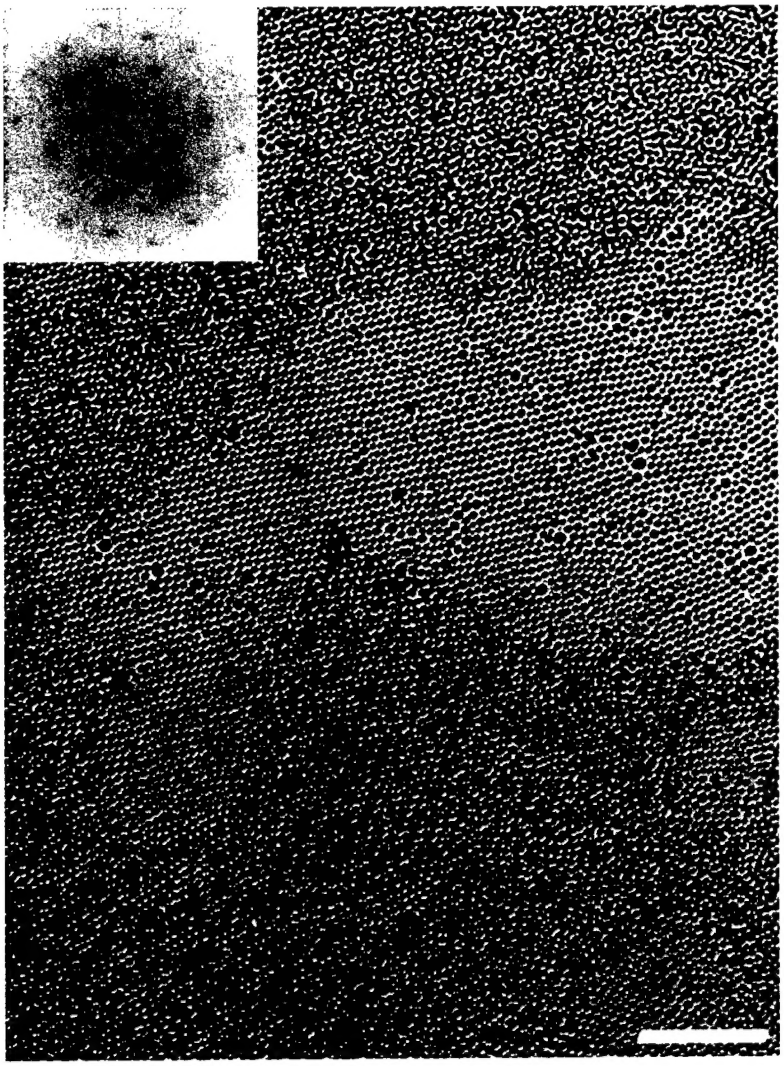
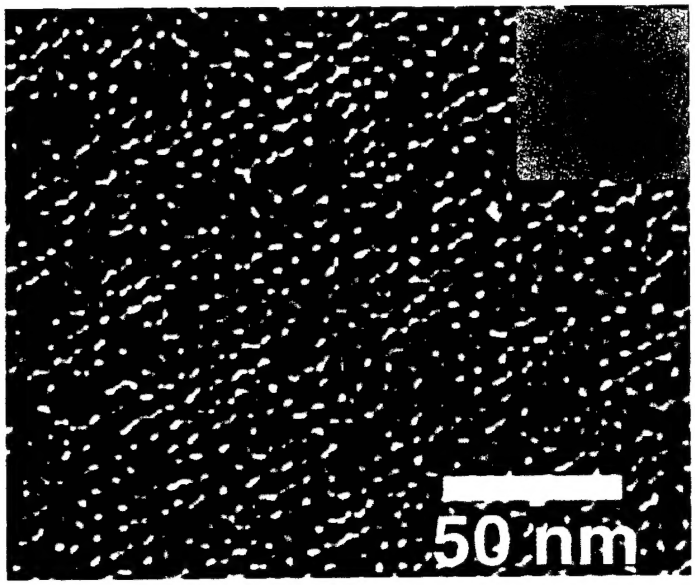
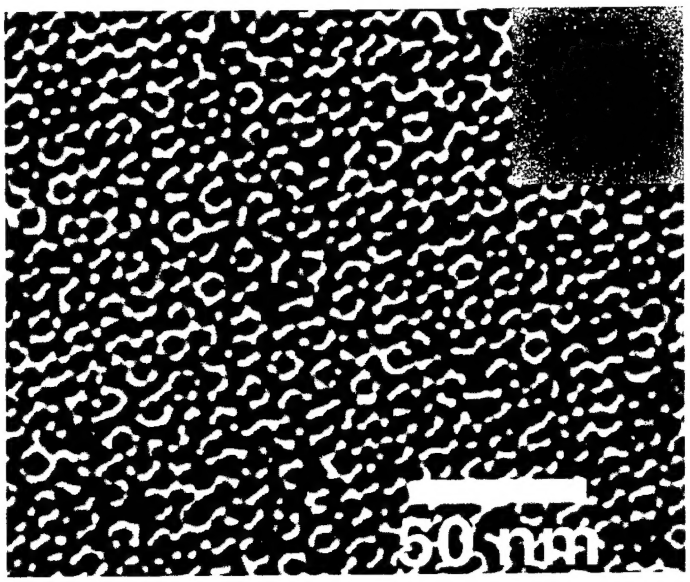


Figure 2

Figure 3



(a)



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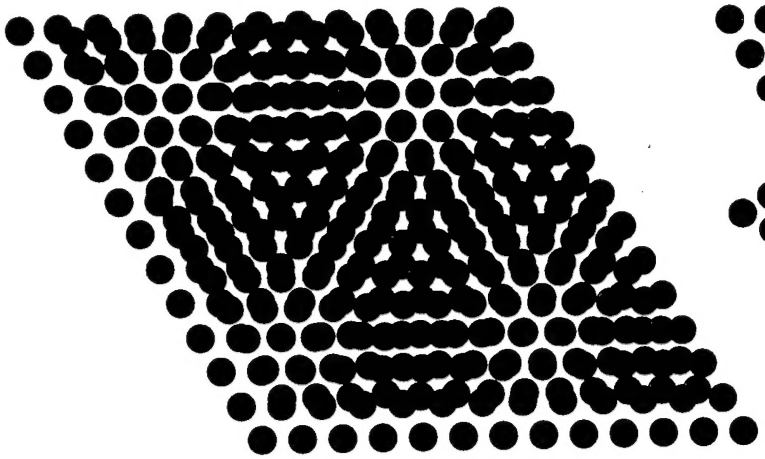
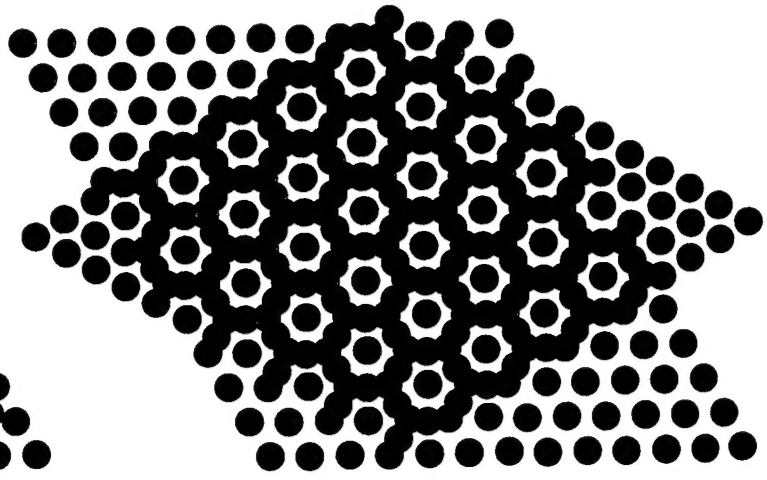


(c)



(d)